Title: **Multifunctional ($NO_x/CO/O_2$) Solid-State Sensor for Coal Combustion Control**

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Objective and Rationale:

There is a tremendous environmental and regulatory need for the monitoring and control of NO_x and CO emissions from coal combustion sources. We have developed solid-state sensor technology that can provide an inexpensive, rugged, solid-state device capable of measuring the concentration of multiple species (such as NO and CO) in coal combustion exhaust. Our goal is to extend this technology to create a single potentiometric (voltage output) sensor that is sensitive to multiple gasses (NO_x, CO, O_2). Such a sensor can be used to improve combustion control, resulting in both improved fuel utilization and reduced emissions.

Our sensors are based on the same technology used in conventional automotive O_2 sensors and thus can be used directly in high temperature exhaust. In our design, all the electrodes are in the same gas stream, significantly reducing fabrication cost. The main obstacle in developing and commercializing low-cost, solid-state, electrochemical sensors for emissions monitoring is attaining the necessary gas selectivity. Specifically, the sensors must exhibit a highly selective response to ppm levels of NO_x and CO in the presence of percent levels of O_2.

The operation of our sensors, that provides the necessary selectivity of NO even in lean-burn (13-17% O_2) exhaust gas, can be explained through a scientific approach we developed called "Differential Electrode Equilibria". By this theory, a difference in electrochemical potential between two electrodes exposed to the same environment will occur if one or both of the electrodes does not achieve thermodynamic equilibrium. In a potentiometric sensor this non-Nernstian response produces a voltage that depends on the concentration of one or more of the species present.

Accomplishments to Date:

We have tested the response of a sensor with a metal oxide electrode that shows selectivity towards NO. The sensor has its highest sensitivity for NO at about 500ºC. It shows selectivity for NO in varying O_2 concentration, under simulated exhaust conditions. Changes in the partial pressures of CO, CO_2, O_2, and NO_2 give much less of a voltage response compared to changes in partial pressure of NO.

At higher temperatures, close to 700ºC, the sensitivity to NO_2 rises significantly. The response stability is also improved at higher temperatures. Study on response to processing conditions shows that the response time is larger for samples with very low coating thickness and samples fired at higher sintering temperatures.

Measurements on the CO sensing elements show highest sensitivity at 500ºC and have very little dependence on variation of O_2 gas concentration. The response appears to be linear within the concentration range 10-1000 ppm. Though the response stability is significant throughout the temperature range 500-700ºC, the sensitivity is highest at lower temperatures.

Future Work:

Further study of the properties of this sensor, including electrode geometry, thickness, and porosity are planned for further optimization of the electrode performance. Future work also involves developing similar type of electrodes with improved selectivity towards CO, NO_2, and O_2. Once this is achieved, work will be focused on creating a multifunctional sensor that utilizes each of these electrodes.

Presentations:

"Multifunctional (NO_x/CO/O_2) Solid-State Sensor for Coal Combustion Control", E.D. Wachsman, The 2002 NETL Sensors and Control Program Portfolio Review and Roadmapping Workshop, October 15-16, 2002, Pittsburgh, PA.

"Selective Potentiometric Detection of NO_X by Differential Electrode Equilibria," E.D. Wachsman, 202nd Meeting of The Electrochemical Society, October 20-24, 2002, Salt Lake City, UT.

"Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x," E.R. Macam, 27th Annual International Conference & Exposition on Advanced Ceramics & Composites, January 27-31, 2003, Cocoa Beach, FL.

"Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x," E.R. Macam, University Scholars Symposium, University of Florida, April 12, 2003,Gainesville, FL.

"Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x," E.R. Macam, 105th Annual Meeting & Exposition of The American Ceramic Society, April 27-30, 2003,Nashville, TN.

"Catalytic and Electrocatalytic Reduction of NO_x on $LaBO_3$ Surfaces,"E.D. Wachsman -Keynote Lecture, NATO Advanced Research Workshop on Mixed Ionic Electronic Conducting Perovskites for Advanced Energy Systems, June 1-5, 2003, Kiev, Ukraine.

Publications and Patents:

"Selective Potentiometric Detection of NO_x by Differential Electrode Equilibria," E.D. Wachsman, *Solid State Ionic Devices III*, Electrochem. Soc., E.D. Wachsman, K.S. Lyons, M. Carolyn, F. Garzon, M. Liu, and J. Stetter, Ed., **2002-26**, 215-221 (2003).

"Solid State Potentiometric Gaseous Oxide Sensor," E. D. Wachsman and A. Azad, July 29, 2003, U.S. Patent No. 6,598,596.

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